

# The Influence on Cement Setting Time and Compression Strength by Adding Stannous Sulphate

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## Abstract

A laboratory test was carried out to investigate the influence of stannous sulphate on the cement setting time and strength. The cement mortar specimens were prepared using grade 32.5 slag cement as binder material and different percentage of stannous sulphate as additive. Experimental results showed that the initial and final setting time of slag cement increased about 3-9 times with the increase of the additive percentage. However, the compression strengths of specimens showed non-monotonic change with the increase of additive ratio implying that an optimal additive percentage exists. The retarding mechanism of stannous sulphate was also explained through Taylor's model.

## Keywords

*Stannous Sulfate; Cement; Setting Time; Compressive Strength; Taylor Model*

## Introduction

Tin salt, as a kind of important industrial products, has been widely used in electroplating, ceramics, plastics and other industries. In recent years, with the further study of tin salt, it was found that tin salt has some influences on the cement setting time, strength, stability, detoxification and the corrosion resistance of concrete (Sing Tsze Yue, 1977; J. Hill, J.H. Sharp\*, 2003; K.K. Sagoe-Crentsil, F.P. Glasser, V.T. Yilmaz, 2008; Rina S. Vaity, K. J. Somaiya, 2011.). Nabajyoti Saikia(2011) found that 0.5% and 1% of tin salt could promote the hydration influence of C<sub>3</sub>A, while 2% of tin salt has inhibitory influence in the early stage hydration (< 3 h). J.Hill (2003) pointed out that SnCl<sub>2</sub> could block the setting time of cement. Sing Tsze(1977) made the point that the stannous sulfate has the effect on the cement hydration hardening rate and setting time.

Stannous sulfate as an important part in the tin salt, its influence on cement has attracted more and more attention. To study the relationship between stannous

sulfate and cement setting time and strength, cement mortar specimens with water cement ratio of 0.5 were carried out by using the grade 32.5 slag cement as the binder and stannous sulphate as additive. On the basis of experimental results, this paper used the Taylor model to explain the influence of stannous sulphate on the cement setting time from the view point of the microscopic structure.

## The Experiment

### *The Experimental Design*

The experiment was divided into two groups, see table 1 and table 2, the first of which is to investigate the influence of stannous sulphate on the setting time of cement slurry net; while the other is to study the influence of stannous sulfate on the compressive strength of mortar specimens.

TABLE 1 THE EXPERIMENT GROUP OF CEMENT PASTE (g)

Group	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>
slag cement	500	497.5	495	485
stannous sulfate	0	2.5	5	15

TABLE 2 THE EXPERIMENT GROUP OF CEMENT MORTAR (G)

Group	stannous sulfate	cement	water	standard sand
A <sub>2</sub>	0	450	225	1350
B <sub>2</sub>	2.3	447.7	225	1350
C <sub>2</sub>	4.5	445.5	225	1350
D <sub>2</sub>	13.5	436.5	225	1350

*The actual quality of standard sand has some errors, all among the 1350±5 g.*

### 1) The Experiment Materials

- Stannous sulfate comes from Chengdu gracia chemical technology co., LTD., (AR) purity ( $\geq 99.0\%$ ), HCl insoluble ( $\leq 0.005\%$ ), chloride (Cl<sup>-</sup>) : ( $\leq 0.005\%$ ), iron(Fe): ( $\leq 0.005\%$ ).
- Standard sand comes from China ISO Standard Sand co.,LTD. The production of standard sand,

particle size: 0.25~0.65 mm,  $\text{SiO}_2 > 96\%$ , the silt content (including soluble salts)  $\leq 0.20\%$ , ignition loss  $\leq 0.40\%$

- Water is tap water in Kunming.
- Cement uses the "SHILIN" brand cement, fineness is 0.60, specific surface area is 378  $\text{m}^2/\text{kg}$ . Its chemical compositions of concrete are shown in table 3:

TABLE 3 CHEMICAL COMPOSITION TABLE OF CEMENT (%)

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$
33.72	13.55	2.11	41.95
$\text{MgO}$	$\text{SO}_3$	$\text{Cl}^-$	
3.22	2.28	0.009	

## 2) The Process of Experiment.

- Mixing neat cement paste

Neat cement pastes of Group A<sub>1</sub> are mixed according to Ref.[7] (GB/T 1346-2011). Dissolve the stannous sulfate of B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub> into some water, then add the solution into pot respectively, the mixing of neat cement pastes as Group A<sub>1</sub>.

- Measuring standard consistency water consumption

Standard consistency water consumption of Group A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub> are measured according to Ref.[7] (GB/T 1346-2011).

- Measuring the setting time

The initial time and final setting time of Group A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub> are measured according to Ref.[7] (GB/T 1346-2011).

- Measuring compressive strength

Based on the Table 2, cement mortars are produced with a size of 40 mm×40 mm×160 mm. Except Group D<sub>2</sub>, all mortars are put in standard curing box (constant temperature 20°C, relative humidity 95%) for 24 hours, the mortars of D<sub>2</sub> are 48 hours. Then curing in water, the curing periods are divided into 3d, 14d and 28d.

## The Experimental Results

### 1) Superficial Analysis

At the beginning of mixing, the test specimens added with 3% of stannous sulfate happen to the phenomenon of "false setting" that is recorded by photographs (Figure 1 and Figure 2). After mixing lasting for 15 s, the powders and the stannous sulfate solution start a sharp reaction and generate spherical particles, and the batter presents a dry

state. About 40 s, this kind of situation disappears, the batter presents thickened. The other groups do not happen to this phenomenon. This phenomenon may be attributed to higher dosage of stannous sulfate, because it can dissolves out more sulfuric acid root ion in aqueous solution. While the higher sulfuric acid root can response with calcium ion rapidly in the early hydration, which consumes a large amount of water and generates the insoluble crystallization, finally hinders the hydration of cement. Because of the addition of external force, it breaks the insoluble crystallization barriers, leading to the hydration reaction that continues to react, and the mixing at about 40 s becomes "normal".



FIGURE 1 GROUP D<sub>1</sub> STIRRING ABOUT 15s



FIGURE 2 GROUP D<sub>1</sub> STIRRING ABOUT 40s

### 2) Mortar Maintenance Phase

Take them out and wipe the surface water when the cement mortars are soaked in water 3d, see figure 3 and figure 4. From the photos, it can be learnt that Group A<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub> are intact and no cracks, Group D<sub>2</sub> occurs long cracks on the surface and close the lateral surface of the block. This phenomenon should contribute to the constraints. High dosage of stannous sulfate in cement produces more ettringite than normal condition, while the ettringite generates a certain amount of internal forces on the cement stones. Due to the mould wall, the surfaces of cement except the top surface form densely. Without the constraints, the

top surface has lots of flaws when it sets, and the edges are often the weakness of the block. Thus, it will produce lots of cracks along with edges under the internal forces.

FIGURE 3 GROUP A<sub>2</sub>,B<sub>2</sub>,C<sub>2</sub> CURING 3dFIGURE 4 GROUP D<sub>2</sub> CURING 3d

## The Analysis

### Standard Consistency Water Consumption

On the basis of experiment, the standard consistency water consumption of each group is shown in the following table 4,

TABLE 4 STANDARD CONSISTENCY WATER OF EACH GROUP

Test Group	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>
water consumption(ml)	131	129	128	134

As the errors of water consumption are within 2.29%, and with the admixtures performance indicators, the adding of stannous sulphate does not achieve the effect of water reducing agent. Regarding the errors due to the temperature, the accuracy of the instrument and artificial operation, it can be thought that the stannous sulfate does not have significant influence on the water consumption.

### The Setting Time

On the basis of experiment, the setting time of each Group is shown in the following table 5,

TABLE 5 THE SETTING TIME

Test Group	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>
Initial Setting Time(min)	297	855	1220	1812
Final Setting Time(min)	364	937	1396	2116

To have a better observation about the result, using the polynomial approximation fitting to link test data, see figure 5 and figure 6.

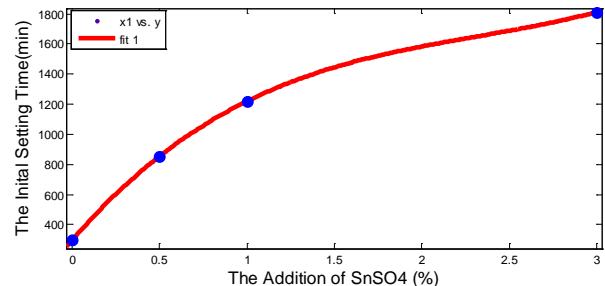


FIGURE 5 THE FITTING CURVE OF INITIAL SETTING TIME

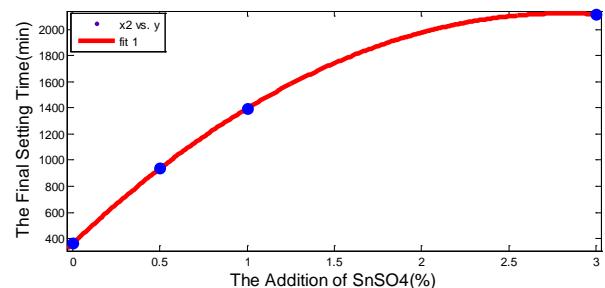


FIGURE 6 THE FITTING CURVE OF FINAL SETTING TIME

From the above, it can be seen that the setting time performs an increasing rate with the increase of the stannous sulfate percentage. Adding 0.5% of stannous sulfate can improve the setting time about 3 times, and 1% is about 4 times, up to 3% is 7 to 9 times. The setting time may grow flat when more than 3% of stannous sulphate are added from the trend.

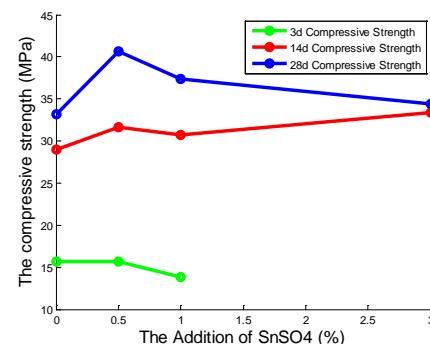


FIGURE 7 COMPRESSION STRENGTH

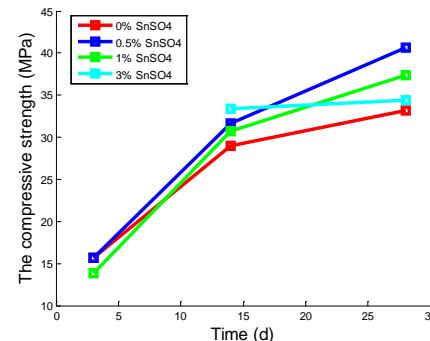


FIGURE 8 COMPRESSION STRENGTH

### The Compressive Strength

To have a better display about the influence of stannous sulfate, the relationships of curing period and compressive strength are shown in Fig.7, and the relationships of the stannous sulfate percentage and compressive strength are shown in Fig.8.

The compressive strengths of cements don't manifest the growth tend of setting time in the Figure 7. In the conservation process, the strengths of Group B<sub>2</sub> are higher than those of other Groups, especially at the age of 28d. The growth rate of strength in the Group B<sub>2</sub> and C<sub>2</sub> are higher than that in Group A<sub>2</sub> from 3d to 28d in Figure 8, however, Group D<sub>2</sub>'s rate is lower than Group A<sub>2</sub> from 14d to 28d. This phenomenon may contribute to the crocks in the Group D<sub>2</sub>, meanwhile, it shows that overweight stannous sulfate may be harmful to cement. All of them imply that an optimal additive percentage may exist, and it needs to be studied in the future.

### The Retarding Mechanism

At present, there are main four kinds of the retarding mechanism: adsorption theory, complexes generated theory, sedimentation theory and calcium hydroxide crystal nucleation theory (Zhao Hongyi, 2007). However, different kinds of retarders could not be explained by one of the theories. From macro level of stannous sulfate retarding action, it can be divided into the following stages: 1) Stannous sulfate dissolves into water and performs lots of sulfuric acid root ion, when the sulfuric acid root ion happens to C<sub>3</sub>A, they react quickly and create the ettringite. The ettringite could not dissolve due to the high concentrations of sulfuric acid root ion in the liquid phase. Then it can form a locking layer on the surface of C<sub>3</sub>S, preventing the hydration of C<sub>3</sub>S. At the same time, tin ions react with calcium ions quickly in the cement system, reforming the complex salt-CaSn(OH)<sub>6</sub>. The complex salt cloud suppresses the Ca<sup>2+</sup> concentration and then prevents the formation of cement hydration phase in the early stage. 2) As the cement continue hydrating, the sulfuric acid root ion and tin ions hydrate with calcium silicate to form C-S-H slowly. As the C-S-H phase formation is the reason of setting time, it is necessary to study the mechanism between stannous sulfate and C - S - H (J.Bensted, P.Banes, 2001).

Tin ion and C-S-H will form a kind of hinge of the Sn-Si-O in the end of the chain of silicon eventually (Isabellbonhoure et al., 2003). The setting time of cement may be related to the formation of the hinge,

because some researchers have showed that cement retardings are associated with the induction period of C<sub>3</sub>S hydration (J.Bensted, P.Banes, 2001). C<sub>3</sub>S phase may become the metastable state (C-S-H (m)) with the addition of admixtures, and the C-S-H (m) can destroy the dynamic equilibrium between C<sub>3</sub>S dissolved and "normal" C-S-H precipitation, thus extending induction period of C<sub>3</sub>S, and the setting time of cement finally (Gartner et al., 1989). As Sn-Si-O hinge destroys the dynamic equilibrium of C-S-H, it is necessary to study the formation of the Sn-Si-O which was explained in this paper by Taylor model.

The C-S-H is layer structure, in which most of the layers are structurally imperfect ones of jennite (Ca<sub>9</sub>Si<sub>6</sub>O<sub>32</sub>H<sub>22</sub>), and other are similarly related to 1.4-nm tobermorite (Ca<sub>9</sub>Si<sub>6</sub>O<sub>26</sub>H<sub>18</sub>). In both 1.4-nm tobermorite and jennite, the silicate chains are in theory, infinitely long, and kinked so as to repeat at intervals of three tetrahedrals (Fig.7)(HARRY F.w., TAYLOR\*, 1986). In each Group of three tetrahedrals, two share O atoms with the center, Ca-O part of the layer; the third, which does not, will be called a "bridging" tetrahedron.

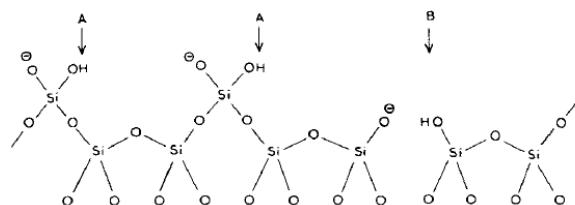


FIGURE 7 TAYLOR MODEL

In both 1.4-nm tobermorite and jennite, there appears to be one H atom attached to each bridging tetrahedron (Fig.1(A)). When a bridging tetrahedron is omitted, one of the broken ends of the chain carries a H atom and the other does not (Fig.1(B)). As the H atom always shows in the end of the chain, it is more likely to absorb the tin ion in the solution and form new bonds. That may be the reason why the Sn - Si - O hinges always appear in the end of chain.

### Conclusion

On the basis of the experiment, it can be found out that stannous sulfate has a great influence on slag Portland cement: the initial and final setting time of slag cement increase about 3-9 times with the increase of the additive percentage; however, the strength of cement mortar becomes weaker in the early stage, but stronger in the later hydration, which implies that stannous sulfate could be a good retarder without affecting the excellent properties of cement. At the same time, there may have an optimal value between the quantity of stannous sulfate added and strength, and it need to be

studied in the future. It should be worth noting that the excess of stannous sulfate on the cement could produce adverse reactions, because it can produce a lot of ettringite in the late of hydration and harm for the cement.

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